

AD-782 953

CHARGE NEUTRALIZATION AND ELECTRON  
SCAVENGING IN IRRADIATED DIELECTRIC  
LIQUIDS

George A. Ausman, Jr.

Harry Diamond Laboratories

Prepared for:

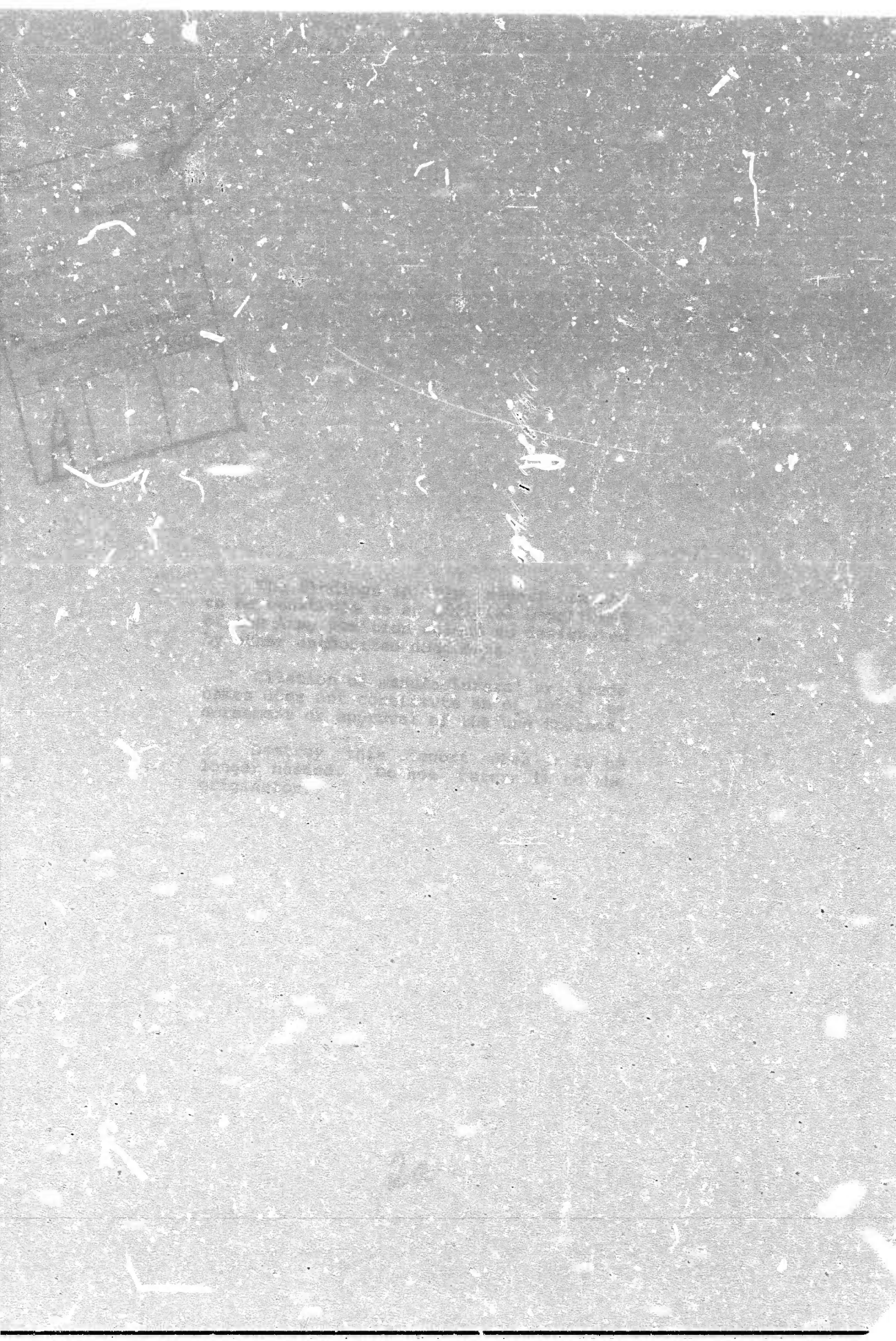
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER HDL-TR-1662	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle)  CHARGE NEUTRALIZATION AND ELECTRON SCAVENGING IN IRRADIATED DIELECTRIC LIQUIDS		5. TYPE OF REPORT & PERIOD COVERED  TECHNICAL REPORT
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s)  GEORGE A. AUSMAN, Jr.		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS  Harry Diamond Laboratories Washington, DC 20305		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Program Element: 6.11.02.H Subtask No. TA008 Work Unit: 013A9
11. CONTROLLING OFFICE NAME AND ADDRESS Director Defense Nuclear Agency Washington, DC 20305		12. REPORT DATE APRIL 1974
		13. NUMBER OF PAGES 20
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report)  Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)  APPROVED FOR PUBLIC RELEASE: DISTRIBUTION UNLIMITED.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES  THIS RESEARCH IS SPONSORED BY THE DEFENSE NUCLEAR AGENCY UNDER NWER SUBTASK TA008.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)  Dielectric Radiation effects Scavenging Photochemistry		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  The Smoluchowski equation, which governs the motion of an isolated electron-ion pair undergoing mutual coulomb attraction and random walk in a dielectric medium, is modified to include electron scavenging. The solution is obtained numerically for values of time ranging over five orders of magnitude. The results are in accord with recent time-dependent conductivity measurements on n-hexane following radiation-induced ionization. To our knowledge, this is the first report of a direct comparison of theory with time-dependent conductivity data in the nanosecond regime on samples with		

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relatively low scavenger concentrations.

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## TABLE OF CONTENTS

<u>Section</u>	<u>Title</u>	<u>Page</u>
1	INTRODUCTION . . . . .	4
2	MATHEMATICAL FORMULATION . . . . .	6
3	RESULTS AND DISCUSSION . . . . .	11
	LITERATURE CITED . . . . .	18

## LIST OF ILLUSTRATIONS

<u>Figure</u>	<u>Title</u>	<u>Page</u>
1	Probability density of electron as a function of distance from the positively charged ion at various times . . . . .	12
2	Radial probability distribution as a function of distance from the positively charged ion at various times . . . . .	12
3	Fraction of electrons remaining unneutralized as a function of time. Curve I is Mozumder's prescribed diffusion approximation for an initial delta-function distribution at 80Å; curve II represents the present results for the same initial condition; curve III is our result for a gaussian distribution centered at 80Å with $\sigma = 20$ Å. . . . .	13
4	Fraction of unneutralized electrons remaining as a function of time for various levels of scavenger concentration. . . . .	14
5	Fraction of electrons remaining unneutralized and unscavenged as a function of time. In the absence of scavengers ( $\lambda = 0$ ) the upper dashed curve is the prescribed diffusion solution to the Smoluchowski equation and the solid curve is our numerical solution. The lower solid curve is our solution in the presence of scavengers . . . . .	14
6	Decay of electrons and cations and growth of anions as function of time for $\lambda = 2 \times 10^7 \text{ sec}^{-1}$ . . . . .	15
7	Fraction of electrons, anions, and cations remaining unneutralized, weighted by the ratio of the mobility of each species to the electron mobility. The solid curve represents the sum of the three contributions and the circles represent the conductivity data of Conrad. . . . .	16

## 1. INTRODUCTION

In conjunction with experimental studies of radiation-induced conductivity in dielectric materials being conducted at the Harry Diamond Laboratories, theoretical efforts have been directed toward describing the dynamics of the recombination processes governing the decay of the ionization produced in condensed media by irradiation. This report presents results of calculations of the time-dependent neutralization of an isolated electron-ion pair in a condensed dielectric medium for values of time ranging from times shorter than can presently be measured experimentally to those earliest measureable. These initial recombination processes determine the ultimate yield of quasi-free charge carriers present at times accessible to experimental measurement. The present work considers the neutralization of isolated electron-ion pairs in a condensed dielectric medium for two cases: (1) no chemical impurities acting as charge scavengers are present; (2) charge scavengers are present. Structural effects characteristic of the solid state are neglected. Thus, the model is most applicable to pure dielectric liquids.

We assume that, following irradiation and subsequent thermalization of the electrons, the dielectric medium can be treated as consisting of isolated electron-ion pairs. Under this assumption the recombination at early times can be described by considering a single isolated electron-ion pair. The restriction of the theory to the case of isolated electron-ion pairs, although an oversimplification, is still of practical interest since it should apply reasonably well to ionization produced by low LET (linear energy transfer), high-energy radiation. The motion of the pair of ions of opposite signs is governed both by their mutual coulomb attraction and random walk in the dielectric medium. It is assumed that the random walk can be approximated by the diffusion equation. Einstein<sup>1</sup> showed that the diffusion approximation is valid when the times of interest are much larger than the relaxation time characteristic of Brownian motion. This result was obtained by Einstein from the general Fokker-Planck<sup>2</sup> equation for the probability distribution function in six-dimensional phase space. This equation is not separable in position and velocity unless the time intervals of interest,  $\Delta t$ , satisfy  $\Delta t \gg Dm/kT$  where  $D$  is the diffusion coefficient of the particle of mass  $m$ ,  $k$  is the Boltzman constant, and  $T$  is temperature.<sup>2</sup> The time  $Dm/kT$  is the time required for the particles to traverse a mean free path of the order of  $(D^2m/kT)^{1/2}$ . The diffusion equation was generalized by Smoluchowski<sup>3</sup> to include the effect of an external field. In order for the equation to apply to configuration space independently of velocity space it is required that the Maxwellian velocity distribution not be seriously affected by the external field. This requirement is met if the variation of the force  $F(\vec{r})$  is small over a mean free path.<sup>2</sup> The problem of the isolated electron-ion pair meets this condition provided the electron-ion separation is not too small, since the variation of the coulomb force over the distance  $(D^2m/kt)^{1/2}$  becomes too great at small separations.

<sup>1</sup>Einstein, A. Ann. Physik 17, 549 (1905); 19, 371 (1906).

<sup>2</sup>Chandrasekhar, S., Rev. Mod. Phys. 15, 1 (1943).

<sup>3</sup>von Smoluchowski, M., Ann. Physik 21, 756 (1906).

Onsager<sup>4</sup> was the first to solve the Smoluchowski equation for a pair of ions in a dielectric medium. He derived the result that, in the steady state, i.e., in the limit  $t \rightarrow \infty$ , the probability that the pair will escape mutual neutralization is given by  $\exp(-r_c/r_i)$ , where  $r_c = e^2/\epsilon kT$  and  $r_i$  is the initial separation of the electron and positive ion. However, the Onsager theory is a steady-state theory and does not describe the dynamics of the process; i.e., how fast or slow the steady-state value is obtained.

Recently there has been an increasing interest in obtaining the time-dependence of the evolution of the system to the steady state. Attempts have been made to obtain approximate solutions for finite times. The most recent analytical approach is the work performed by Mozumder.<sup>5</sup> He used the method of "prescribed diffusion." In this method a solution is first obtained to the simple diffusion equation which results when the force term is set equal to zero in the Smoluchowski equation. It is then assumed that the solution to the Smoluchowski equation can be approximated by multiplying the solution to the diffusion equation by some unknown function of time. This assumed solution is then substituted into the original Smoluchowski equation and a solvable equation for the unknown function of time is obtained. The first attempt to solve the Smoluchowski equation directly by numerical methods, without resorting to any analytical approximations, was that of Ludwig.<sup>6</sup> He used an analog computer method. By noting the similarity of the Smoluchowski equation with the differential equations describing time and position dependence of a dc voltage along a one-dimensional tapered electric line, he was able to set up an analog method for the solution by identifying the parameters of the Smoluchowski equation with voltages, resistances, and capacitances in the equivalent electrical circuit. The actual solution, however, was carried out using a digital computer program ECAP (Electronic Circuit Analysis Program) which is specifically designed for electric circuit analysis. By comparing his results with those obtained by Mozumder, using "prescribed diffusion," Ludwig found that his results predicted a faster rate of recombination than predicted by Mozumder's method. Quite recently Abell et al<sup>7</sup> have applied a Laplace transform method to the numerical solution of the Smoluchowski equation. Their primary interest was in deriving the scavenging probability, however, the inverse Laplace transform of their solution also gives the time-dependent solution. Their results appear to be in accord with Ludwig's results and demonstrate that the numerical solution is in good agreement with the prescribed diffusion method at long times.

In addition to extending the work of others on the neutralization of an isolated electron-ion pair, we consider the effect of the presence of a solute. In this case the neutralization process competes

<sup>4</sup>Onsager, L., Phys. Rev. 54, 554 (1938).

<sup>5</sup>Mozumder, A., J. Chem. Phys. 48, 1659 (1968).

<sup>6</sup>Ludwig, P. K., J. Chem. Phys. 50, 1787 (1969).

<sup>7</sup>Abell, G. C., A. Mozumder, and J. J. Magee, J. Chem. Phys. 56, 5422 (1972).



with the possible reaction of one of the charged species with the solute. This reaction with the solute is commonly referred to as charge scavenging and the solute itself is called the scavenger. Recent studies<sup>8-12</sup> of the neutralization and scavenging of electrons following radiation-induced ionization in liquid hydrocarbon have involved the determination of the product yield as a function of scavenger concentration. Theoretical work<sup>5,7,12</sup> has followed the procedure of either obtaining approximate solutions to the Smoluchowski equation for the time dependence of neutralization and then relating the Laplace transform to experimental scavenging studies, or numerically solving the Laplace transformed Smoluchowski equation. Good quantitative agreement between theory and experiment on scavenging studies was recently obtained by Abell and Funabashi<sup>13</sup> using the latter method. We have taken another approach. We have compared numerical solutions of the time-dependent Smoluchowski equation directly with time-dependent conductivity data that have recently been obtained in the nanosecond time regime.<sup>14</sup> When electron scavengers are present, a new low-mobility charge species, the anion, is created which contributes to the conductivity at later times. Good agreement between theory and experiment is obtained. Also, our solution to the Smoluchowski equation should be valid at early times where the "prescribed diffusion" approximation used by Mozumder<sup>5</sup> is not appropriate and is in excellent agreement with Mozumder's result at long times — the region of validity of the "prescribed diffusion" approximation.

In section 2 we present the mathematical formulation of the problem. It is shown how the Smoluchowski equation is modified to include the effect of scavengers on the electron distribution, and a brief description of the numerical method of solution is presented. As the electrons are trapped by the scavengers, a new negatively charged species (the anion) is created. The equation governing the probability density of the anions is presented, and we indicate how the coupled partial-differential equations governing the electron and anion time-dependent distributions are solved.

In section 3 we present the solutions and discuss the results.

## 2. MATHEMATICAL FORMULATION

We assume that there are two isolated particles interacting via the coulomb force in a dielectric medium. One particle (the positive ion) is

<sup>5</sup>Mozumder, A., J. Chem. Phys. 48, 1659 (1968).

<sup>7</sup>Abell, G. C., A. Mozumder, and J. J. Magee, J. Chem. Phys. 56, 5422 (1972).

<sup>8</sup>Rzad, S. J., P. P. Infelta, J. M. Warman and R. H. Schuler, J. Chem. Phys. 52, 3971 (1970).

<sup>9</sup>Rzad, S. J. and J. M. Warman, J. Chem. Phys. 49, 2861 (1969).

<sup>10</sup>Rzad, S. J., P. P. Infelta, J. M. Warman and R. H. Schuler, J. Chem. Phys. 50, 5074 (1969).

<sup>11</sup>Thomas, R. K., K. Johnson, T. Klippert and R. Lowers, J. Chem. Phys. 48, 1508 (1968).

<sup>12</sup>Hummel, A., J. Chem. Phys. 49, 4840 (1968).

<sup>13</sup>Abell, G. C. and K. Funabashi, J. Chem. Phys. 58, 1079 (1973).

<sup>14</sup>Conrad, E. E. and J. Silverman, J. Chem. Phys. 51, 450 (1969); See also E. E. Conrad, Ph.D. thesis, University of Maryland 1970 (unpublished).



assumed to be fixed at the origin and the other (the electron) is free to undergo Brownian motion with respect to the first ion. We represent by  $P_0(\vec{r}, t)$  the probability density of the diffusing particle so that  $P_0(\vec{r}, t) r^2 dr d\Omega$  is the probability of finding the two particles separated by a distance between  $r$  and  $r + dr$  in the solid angle between  $\Omega$  and  $\Omega + d\Omega$  at time  $t$ . The Smoluchowski equation for the probability density  $P_0(\vec{r}, t)$  of the electron can be written as

$$\frac{\partial P_0(\vec{r}, t)}{\partial t} = D\{\nabla^2 P_0(\vec{r}, t) - (e/kT) \nabla \cdot [\vec{E} P_0(\vec{r}, t)]\} \quad (1)$$

where  $\vec{E}$  is the electrostatic field and  $D$  is the relative diffusion coefficient. In the presence of scavengers an additional term,  $-k_s C_s P(\vec{r}, t)$ , must be added to the right side of equation (1), where  $k_s$  is the rate of scavenger reaction and  $C_s$  is the concentration of scavengers:

$$\frac{\partial P(\vec{r}, t)}{\partial t} = D\{\nabla^2 P(\vec{r}, t) - (e/kT) \nabla \cdot [\vec{E} P(\vec{r}, t)]\} - \lambda P(\vec{r}, t), \quad (2)$$

where we have set  $\lambda = k_s C_s$ . It is easily shown that  $P$  and  $P_0$  are related by

$$P(\vec{r}, t) = P_0(\vec{r}, t) \exp(-\lambda t). \quad (3)$$

Since  $E$  is derivable from a potential,  $U(r) = -e^2/\epsilon r$ , which is a function only of the distance between the electron and positive ion, the equation for  $P(r, t)$  in the presence of scavengers becomes

$$\frac{\partial P(r, t)}{\partial t} = D\left\{\frac{\partial^2 P}{\partial r^2} + \left(\frac{2}{r} + \frac{r_c}{r^2}\right) \frac{\partial P}{\partial r}\right\} - \lambda P(r, t), \quad (r \neq 0), \quad (4)$$

where we have set  $r_c = e^2/\epsilon kT$ . We neglect depletion of the solute by treating  $\lambda$  as a constant. This approximation effectively replaces the second-order scavenging process by a pseudo-first-order process.

Equation (4) was solved numerically by converting the differential equation to a system of difference equations for the variables  $r$  and  $t$ . The integrals were performed with the aid of an IBM 360/91 computer using a fourth-order Runge-Kutta integration technique. Double-precision arithmetic was used throughout the calculation to maintain numerical stability out to long times. To avoid the problem (discussed in the introduction) of small separations of the electron-ion pair, we arbitrarily introduce a "reaction radius"  $r_0$  as Ludwig (ref 6) has done in a similar calculation. Outside this radius the Smoluchowski equation is valid. For separation distances less than  $r_0$  it is assumed that the electron-ion pair is neutralized. The choice of  $r_0$  is somewhat arbitrary. We follow Ludwig and choose  $r_0$  to be approximately that separation for which the change in potential energy, when the ions approach by one mean-free-path, is equal to  $kT$ . For our assumed value of dielectric constant

<sup>6</sup>Ludwig, P. K., J. Chem. Phys. 50, 1787 (1969).

$\epsilon = 2$  and a mean-free-path of  $2 \text{ \AA}$ , the resulting  $r_0$  is about  $25 \text{ \AA}$ . Ludwig used a value of  $28 \text{ \AA}$  in his calculations. In order to initially correlate our results with his, we also chose the value  $28 \text{ \AA}$  for  $r_0$ . We later found that the results are quite insensitive to this choice, since much smaller values of  $r_0$  led to approximately the same results.

The boundary conditions on the probability density are therefore as follows:

$$P(r_0, t) = 0, P(\infty, t) = P(\infty, 0), \quad (5)$$

i.e., very far from the origin, the diffusing species remains at the initial value of concentration. For practical calculational purposes " $\infty$ " is simply taken to be some spacial distance from the origin where  $P(r, t) \approx 0$  (since in our calculations we shall consider only initial distributions for which  $P(\infty, 0) = 0$ ). Since the diffusion term causes a gradual broadening of the probability density with increasing time, the value of  $r$  for which  $P(r, t) \approx 0$  must necessarily increase with time. This is accounted for automatically in the program and will be made more quantitative when we discuss the stability criteria used in the calculation.

A variety of initial conditions were considered. However, the one for which the final correlation with experiment was made is

$$P(r, 0) = \frac{\delta(r-r_i)}{4\pi r^2} \quad (6)$$

For this initial condition it is assumed that the diffusing particle (the electron) is located a distance  $r_i$  from the positive ion at  $t = 0$ . Calculations for initial gaussian distributions were also performed; i.e.,

$$P(r, 0) = \frac{A \exp [-(r-r_i)^2/2\sigma^2]}{4\pi r^2} \quad (7)$$

where  $A$  is a normalization constant chosen such that

$$\int_0^\infty P(r, 0) 4\pi r^2 dr = 1 \quad (8)$$

and  $\sigma$  is a measure of the "width" of the distribution. It should be noted that the delta function distribution, equation (6), automatically satisfies equation (8). The value chosen for  $r_i$  was  $80 \text{ \AA}$  and is based upon calculations performed by Mozumder and Magee.<sup>15</sup> This value for  $r_i$  also gives a value for the Onsager steady-state solution ( $t \rightarrow \infty$ ) which

<sup>15</sup>Mozumder, A. and J. L. Magee, J. Chem. Phys. 47, 939 (1967).

is in good agreement with late-time experimental results on n-hexane (ref 14).

The quantity of direct physical interest is the fraction remaining unneutralized at time  $t$ ,

$$\begin{aligned} f(t) &= \int_0^{\infty} 4\pi r^2 P(r,t) dr \\ &= \int_0^{\infty} 4\pi r^2 P(r,t) dr. \end{aligned} \quad (9)$$

According to the normalization specified by equation (8),  $f(0) = 1$ . As time increases,  $f(t)$  decreases until it approaches the Onsager steady-state value  $\exp(-r_c/r_i)$  as  $t \rightarrow \infty$ .

Before solving equation (4) the dimensionless variables  $x = r/a$  and  $T_0 = (D/a^2)t$  were introduced, where  $a$  was chosen for convenience to be 4 Å. The diffusion coefficient  $D$  was taken to be approximately characteristic of n-hexane,  $D = 5 \times 10^{-3} \text{ cm}^2/\text{sec}$ . To start with, a mesh size  $\Delta x = 1$  was used. To check convergence with this mesh size, values of  $\Delta x = 0.5$  and  $\Delta x = 2$  were tested. Good agreement was found between the results using different mesh sizes, although the value  $\Delta x = 2$  appeared to be too large. The value  $\Delta x = 1$  was therefore used at the starting mesh size.

We shall use the term "profile" to characterize the array of values  $P(x_i)$  corresponding to the values of the probability density at the points  $x_i$  at a given time  $T$ . This profile is initially ( $T = 0$ ) taken to be either a delta function or a sharply-peaked gaussian. As time increases, this profile tends to become smoother (due to the diffusion term) and eventually peaks near the "sink" at  $r_0$  (due to the attraction to the positive ion). The fact that the profile becomes smoother with time causes problems in the form of round-off errors by the computer operations on the difference equations. If left uncorrected, these round-off errors eventually lead to totally unmeaningful results. To circumvent this problem the mesh size had to be increased periodically when the profile began to smooth out. This was done without changing the total number (50) of mesh points. This increase in mesh size without changing the total number of points used had the effect also of automatically taking care of the problem referred to earlier — namely, that the value of  $r$  for which  $P(r,t) \approx 0$  must necessarily increase with time.

An option was built into the program to make it possible to double the mesh size either at times specified on input cards or at times determined automatically by the relation

$$\Delta T_{\max} \geq \frac{(\Delta x)^2}{2}, \quad (10)$$

<sup>14</sup>Conrad, E. E. and J. Silverman, J. Chem. Phys. 51, 450 (1969); See also E. E. Conrad, Ph.D. thesis, University of Maryland 1970 (unpublished).

where  $\Delta T_{\max}$  is the current value of the maximum step in  $T$  being used in the integration subroutine and  $\Delta x$  is the current spacial mesh size. This relation is equivalent to the relation

$$\Delta t \geq \frac{(\Delta r)^2}{2D} \quad (11)$$

in real space and time. It has been shown<sup>16</sup> that, for the diffusion equation, it is impossible to choose  $\Delta t$  and  $\Delta r$  arbitrarily if a stable solution is to be obtained. The error is bounded if

$$\Delta t \leq \frac{(\Delta r)^2}{2D}. \quad (12)$$

Thus, we cannot increase  $\Delta t$  arbitrarily without also increasing  $\Delta r$ . The stability criterion is automatically taken care of by the doubling procedure.

In the presence of impurities acting as electron scavengers not only is there an additional process competing with neutralization for the removal of electrons (equation (2)), but a new species is created. This new negatively charged ion (anion) is the impurity with a trapped electron. In the simplified model we are considering the equation for the probability density  $P_A(r,t)$  of anions is

$$\frac{\partial P_A}{\partial t} = D' \left[ \frac{\partial^2 P_A}{\partial r^2} + \left( \frac{2}{r} + \frac{r_c}{r^2} \right) \frac{\partial P_A}{\partial r} \right] + \lambda P(r,t), \quad (r \neq 0) \quad (13)$$

where  $D' = D_c + D_A$ .  $D_c$  is the diffusion coefficient for the cations and  $D_A$  is the diffusion coefficient for the anions. It should be noted that this equation is very similar to equation (4) except for the presence of the term  $+ \lambda P(r,t)$ , where  $P(r,t)$  is the electron probability density determined by equation (4). Also, since at  $t = 0$  there are no anions present, the initial condition is

$$P_A(r,0) = 0. \quad (14)$$

The boundary conditions on  $P_A(r,t)$  are the same as those for  $P(r,t)$ , namely

$$P_A(r_0,t) = P_A(\infty,t) = 0. \quad (15)$$

It is possible to first solve equation (4) for  $P(r,t)$  and store these data for future input to equation (13). However, this technique is laborious and it was found to be more efficient to solve equations (4) and (13) simultaneously.

<sup>16</sup>Smith, G. D., "Numerical Solution of Partial Differential Equations," Oxford University Press, New York and London, 1965.

The fraction of anions present at any time  $t$  is given by

$$f_A(t) = \int_{r_0}^{\infty} 4\pi r^2 P_A(r,t) dr. \quad (16)$$

The fraction of cations (positively charged ions) is just

$$f_C(t) = f(t) + f_A(t), \quad (17)$$

by charge conservation.

### 3. RESULTS AND DISCUSSION

Figure 1 gives results of solutions to equation (4) for the case  $\lambda = 0$  (no charge scavengers). Shown are plots of the spacial profiles, at various times, of  $P_0(r,t)$  using  $D = 5 \times 10^{-3} \text{ cm}^2/\text{sec}$  and  $r_i = 80 \text{ \AA}$ .

Initially, the distribution is a line at  $80 \text{ \AA}$  (as a consequence of the assumed delta function distribution at  $t = 0$ ). As time increases the electron distribution broadens due to diffusion and peaks preferentially toward the origin as a result of the attractive coulomb force. Of more direct physical interest is the radial probability distribution,  $4\pi r^2 P(r,t)$ , which is obtained by integrating  $P(r,t)$  over all angles. The quantity  $4\pi r^2 P(r,t) dr$  represents the probability of finding the electron at a distance  $r$  from the parent ion in the interval  $dr$  at time  $t$ . Figure 2 shows the radial probability distribution at various times. Although the curves in figure 2 are close to gaussian in nature, it should also be noted that the tail at large distances from the origin increases with increasing time leading to the finite probability of the ultimate escape of the electron from the positive ion.

The fraction of electrons remaining unneutralized as a function of time is shown in figure 3 for three different solutions. Curve I is the result of Mozumder's prescribed diffusion approximation for the case of an initial delta-function distribution. Curve II is our result for the same initial distribution. Curve III is our result for a gaussian distribution (equation (7)) centered at  $80 \text{ \AA}$  with  $\sigma = 20 \text{ \AA}$ . As can be seen, at early times, our solution predicts a much faster rate of decay for the geminate pair, the half-life for neutralization ( $\sim 1.8 \times 10^{-11} \text{ sec}$ ) being about half that predicted by Mozumder's prescribed diffusion model. Curves II and III differ significantly only at the earliest times, indicating that the results are not very sensitive to the type of initial distribution chosen.

Our results for the time-dependent decay of the geminate pair in the absence of scavengers are in accord with those of Ludwig when the same parameter values are used. However, his solution was restricted to early times and was not extended into the time domain where the prescribed diffusion model could be tested. We have also solved the case  $r_i = 60 \text{ \AA}$ , which was the case considered by Abell et al, and our results

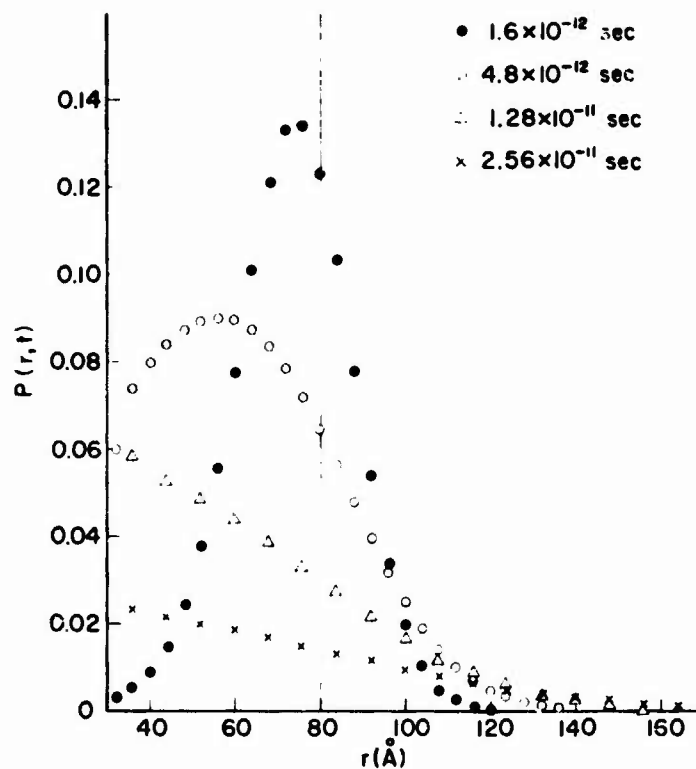


Figure 1. Probability density of electron as a function of distance from the positively charged ion at various times.

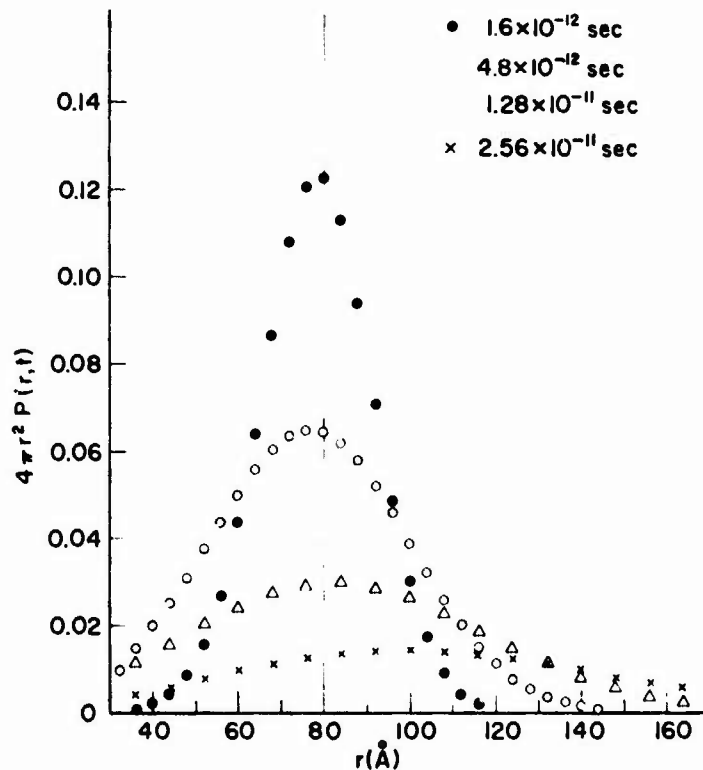


Figure 2. Radial probability distribution as a function of distance from the positively charged ion at various times.

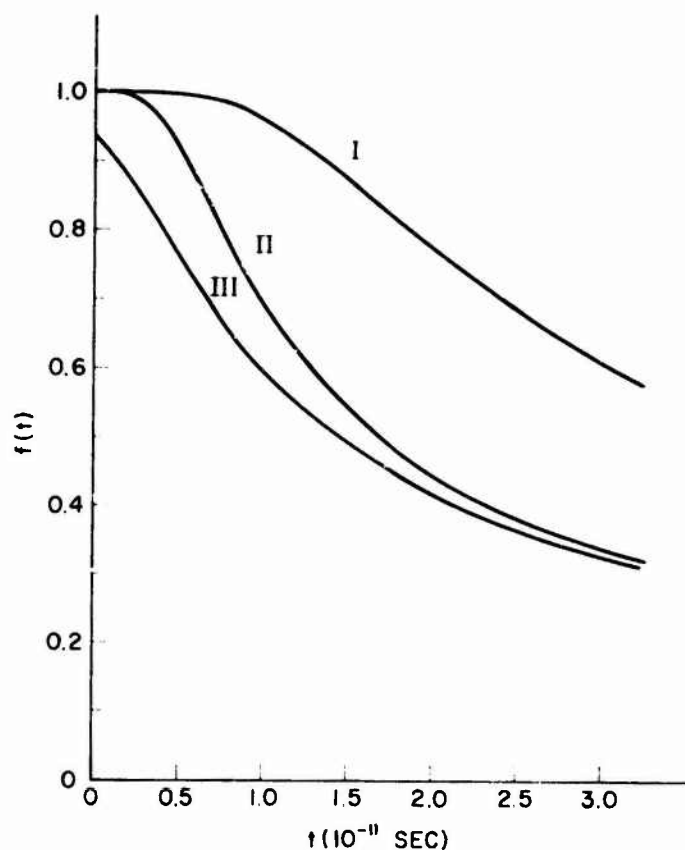


Figure 3. Fraction of electrons remaining unneutralized as a function of time. Curve I is Mozumder's prescribed diffusion approximation for an initial delta-function distribution at 80 Å; curve II represents the present results for the same initial condition; curve III is our result for a gaussian distribution centered at 80 Å with  $\sigma = 20$  Å.

for the time-dependent decay of the geminate pair agree with their work when proper account is taken of the different time scaling due to the use of different diffusion coefficients.

The effect of adding scavengers to the system is shown in figure 4 where a series of curves is shown for various values of  $\lambda = k_s C_s$ . Figure 5 shows results of our solution over a much greater time domain. For the case of no scavengers ( $\lambda = 0$ ), the upper dashed curve is the prescribed diffusion result of Mozumder and the solid curve is the result of the present work. The two solutions coincide (deviations are less than one percent) for  $t > 10^{-8}$  sec, and both approach the Onsager steady-state solution as  $t \rightarrow \infty$ . At early times our solution predicts a much faster rate of decay as mentioned previously. The lower solid curve represents the solution in the presence of scavengers ( $\lambda = 2 \times 10^7 \text{ sec}^{-1}$ ). This curve follows the  $\lambda = 0$  solution out to  $t \sim 10^{-8}$  sec and then begins to fall off very rapidly, reflecting the onset of scavenging. For large times  $F(t) \approx [F(\infty) + At^{-1/2}] \exp(-\lambda t)$ , which is almost a pure exponential decay for large enough times.



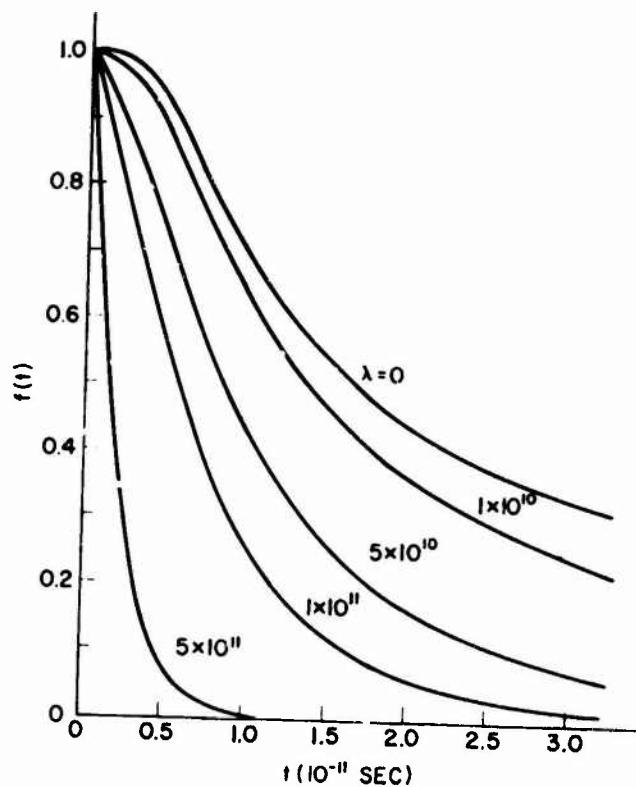


Figure 4. Fraction of unneutralized electrons remaining as a function of time for various levels of scavenger concentration.

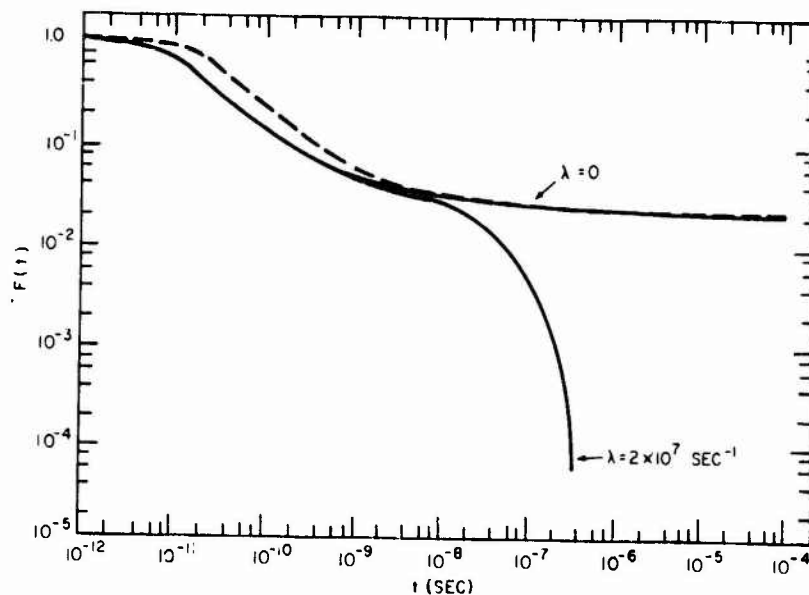


Figure 5. Fraction of electrons remaining unneutralized and unscavenged as a function of time. In the absence of scavengers ( $\lambda = 0$ ) the upper dashed curve is the prescribed diffusion solution to the Smoluchowski equation and the solid curve is our numerical solution. The lower solid curve is our solution in the presence of scavengers.

In order to compare the theory with experimental conductivity data, the presence of the anions and cations must also be taken into account. The evaluations of equations (9), (16) and (17) for the decay of electrons, growth and decay of anions, and decay of cations are shown in figure 6 for the value  $\lambda = 2 \times 10^7 \text{ sec}^{-1}$ . The actual contribution that these three charge species make to the conductivity is given in figure 7, where we have plotted the fraction of each charge species present weighted by the ratio of mobility to the electron mobility. We have taken standard accepted values<sup>17</sup> for the mobility of the cation ( $\mu_C = 6.8 \times 10^{-4} \text{ cm}^2/\text{V-sec}$ ) and anion ( $\mu_A = 1.3 \times 10^{-3} \text{ cm}^2/\text{V-sec}$ ) for n-hexane and have used the previously assumed value of  $0.2 \text{ cm}^2/\text{V-sec}$  for the mobility of the electron. Thus, the relative contribution from the anion is  $(\mu_A/\mu_e) f_A(t) = 6.5 \times 10^{-3} f_A(t)$  and the relative contribution from the cation is  $(\mu_C/\mu_e) f_C(t) = 3.4 \times 10^{-3} f_C(t)$ . The solid line gives the total contribution of all three charge species. For the chosen values of  $D$  and  $\lambda$ , the theory agrees well with the experimental data (indicated by the circles) of Conrad and Silverman (ref 14) for the first stage decay of conductivity in n-hexane following exposure to a flash X-ray pulse. The value for  $\lambda$  corresponds to a lifetime of 50 nsec, the value reported by Conrad and Silverman for the early first-order decay of the conductivity.

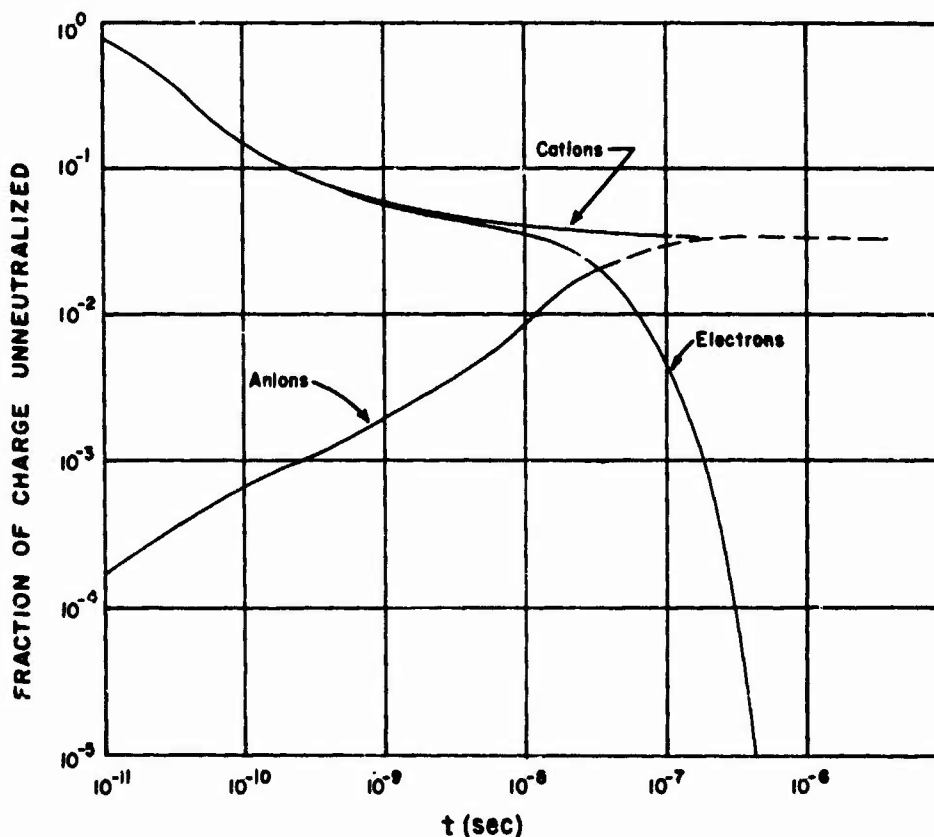


Figure 6. Decay of electrons and cations and growth of anions as function of time for  $\lambda = 2 \times 10^7 \text{ sec}^{-1}$ .

<sup>17</sup>Hummel, A., A. O. Allen, and F. H. Watson, Jr., J. Chem. Phys. **44**, 3431 (1966).

<sup>14</sup>Conrad, E. E. and J. Silverman, J. Chem. Phys. **51**, 450 (1969); See also E. E. Conrad, Ph.D. thesis, University of Maryland 1970 (unpublished).

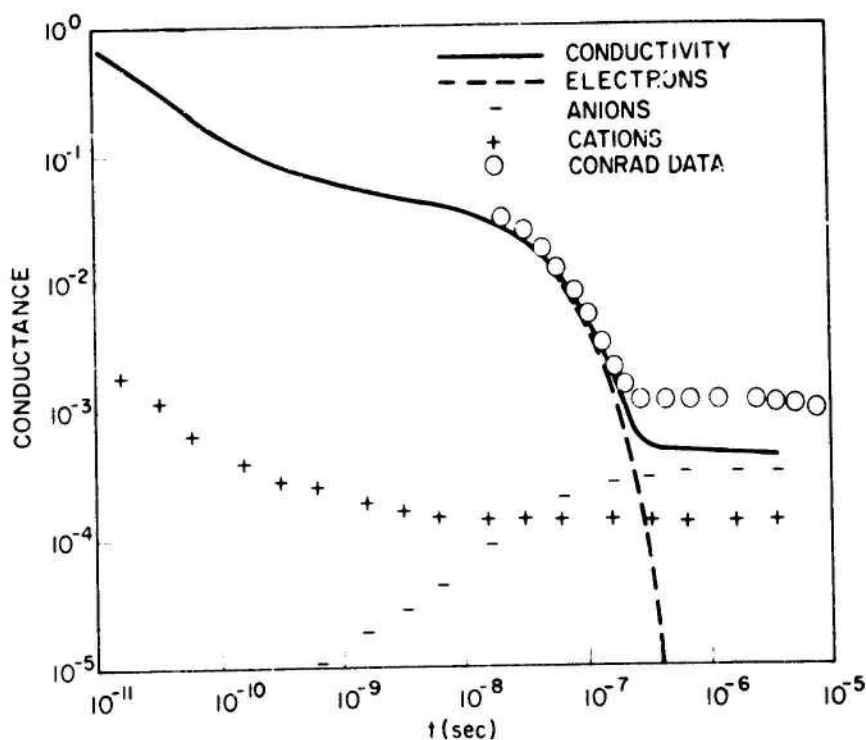


Figure 7. Fraction of electrons, anions, and cations remaining unneutralized weighted by the ratio of the mobility of each species to the electron mobility. The solid curve represents the sum of the three contributions and the circles represent the conductivity data of Conrad.

We have made no attempt to fit experiment in the region following the first stage exponential decay, since no provision has yet been made in the theory to include homogeneous interaction between all the cations and all the anions (bimolecular recombination). The conductivity observed between the exponential decay stage and the onset of nearly pure homogeneous second-order recombination ( $t \sim 100 \mu\text{sec}$ ) is governed by the remaining cations, anions (resulting from scavenged electrons), and, possibly, thermally excited electrons. The discrepancy between theory and experiment in this time region would only be increased if bimolecular recombination were included in the theory. The measured conductivity does not exhibit simple bimolecular recombination in the time range 10-100  $\mu\text{sec}$ . The data suggest that a more mobile species exists in this time range and that a transformation occurs from this species to the slower measured species. Since the more mobile carriers have not been measured yet, we have used the published mobility values. Higher mobilities for the anion and cation would lead to better agreement between theory and experiment.

It is of interest to speculate on how the model presented in this report could be applied to the solid dielectric. The growth of trapped charge in the solid dielectric should be analogous to the growth of anions in the liquid. The only differences would be that the charge trapped in the solid is immobile until thermally released, and the time scale should be shifted to much shorter times in the trap-laden solid relative to the reasonably pure liquid considered here. The conductivity in the solid at observable times is probably due to trap-modulated motion of the electrons, and temperature is probably an important ingredient in any theory of the solid dielectric. Temperature should also be important in any theory of the intermediate time stage in the liquid dielectric which, as mentioned above, we have made no attempt yet to explain.

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